

OFFICE OF NAVAL RESEARCH

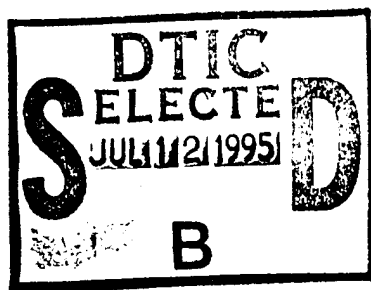
GRANT or CONTRACT: N00014-93-1-0772

R & T Code 313T006

Technical Report #7

Post Cure Effects on Photopolymerization Using Visible Light Initiators

Marino, T.; Long, O. Y.; Neckers, D. C. *Industrial and Engineering Chemistry Research*, in press.



D. C. Neckers
Center for Photochemical Sciences
Dept. of Chemistry
Bowling Green State University
Bowling Green, OHIO 43402

Date Submitted
June 15, 1995

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale, its distribution is unlimited.

19950705 068

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

*The reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 6-15-95	3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Post Cure Effects on Photopolymerization Using Visible Light Initiators			5. FUNDING NUMBERS G N00014-93-J-1921 R & T 313T006	
6. AUTHOR(S) D.C. Neckers			Kenneth Wynne	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Center for Photochemical Sciences Bowling Green State University Bowling Green, Ohio 43402			8. PERFORMING ORGANIZATION REPORT NUMBER 7	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Marino, T.; Long, O. Y.; Neckers, D. C. <i>Industrial and Engineering Chemistry Research</i> , in press.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) In a continuing study of the visible light initiator 2,4-diiodo-3-butoxy-6-fluorone (DIBF), significant post cure was observed in the polymer initially formed from unsaturated polyester resins under both aerobic and anaerobic conditions either in the presence of, or without, ambient light. The extent of post cure varies with the test conditions. A tentative explanation is proposed.				
14. SUBJECT TERMS			15. NUMBER OF PAGE(S)	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

**Post Cure Effects on Photopolymerization
Using Visible Light Initiators**

Thomas Marino* and Oliver Yun Long

Spectra Group Limited

1722 Indianwood Circle, Suite H

Maumee, OHIO 43537

D. C. Neckers

Center for Photochemical Sciences¹

Bowling Green State University

Bowling Green, OHIO 43402

Abstract

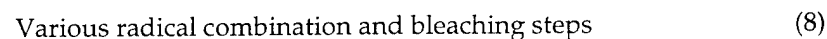
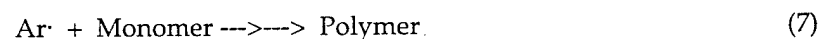
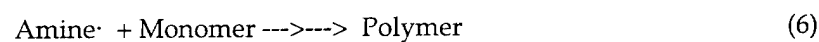
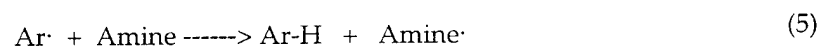
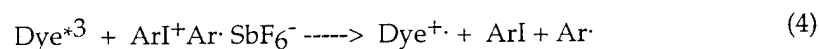
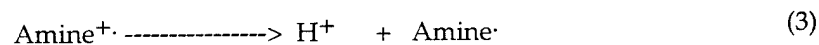
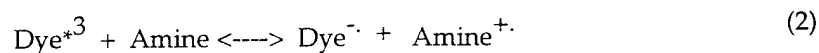
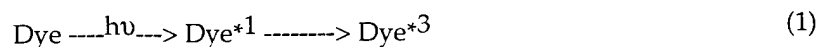
In a continuing study of the visible light initiator 5,7-diiodo-3-butoxy-6-fluorone (DIBF), significant post cure was observed in the polymer initially formed from unsaturated polyester resins under both aerobic and anaerobic conditions either in the presence of, or without, ambient light. The extent of post cure varies with the test conditions. A tentative explanation is proposed.

Introduction

Dyes such as the xanthenes (Eaton, 1986) and, more recently, the fluorones (Neckers, Shi) are effective photoinitiators when used with efficient electron donors such as various tertiary amines. One of a series of new visible initiators, 5,7-diiodo-3-butoxy-6-fluorone (DIBF), absorbs

¹Contribution # from the Center for Photochemical Sciences

of ~30,000 and a low fluorescent quantum yield. During photopolymerization the dye bleaches permitting substantial depth of cure - light penetrates like a hot knife cutting through butter. Additional studies found that when DIBF is combined with (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate (OPPI, available from GE Silicones) and N,N-dimethyl-2,6-diisopropylaniline (DIDMA) as a system, the curing of acrylate resins could be greatly improved (Bi, Neckers, 1994). This new three component system has basically been optimized and is shown to be effective for the curing of unsaturated polyester resins (Hassoon, Neckers, 1995), acrylates and other resins. The mechanism for the DIBF, OPPI and DIDMA initiator system was proposed in previous work (Marino, et al., 1994).



A hybrid "donor/acceptor" mechanism is described in which the excited dye both donates an electron to the onium salt and accepts an electron from the amine. In either case a source of

radicals is generated to initiate cure. Several points are of interest. The dye/amine case results in significant opportunity for back electron transfer diminishing the effectiveness of this process. The dye/onium case, however, results in immediate decomposition of the onium salt with no possibility for back electron transfer. While phenyl radicals can initiate cure their efficiency is poor. The preferred situation is for the phenyl radical to abstract a hydrogen from the amine forming the amine radical which is a very effective initiator. Optimized molar ratios of the dye, onium salt and amine result in a synergistic effect more efficient than dye and either onium or amine alone.

In a continuing study, unsaturated polyester resins which are effectively cured using the DIBF visible initiator system were tested and found to exhibit post cure phenomena. Considering the importance of post cure in understanding and determining final properties in various applications, a systematic study was performed examining several cure and storage conditions.

Experimental

Materials:

All resins were obtained by Owens-Corning Fiberglass, Research Laboratories, Granville, Ohio. The main components are unsaturated polyesters based mainly on terephthalic acid, propylene glycol and maleic anhydride with about 30% styrene. DIBF was synthesized according to established procedures (Neckers, Shi).

Sample Preparation:

DIBF (0.015 g., 3×10^{-5} M) and OPPI (.0384 g, 6×10^{-5} M) were mixed into 2 grams of unsaturated polyester resin. The mixture was stirred for several minutes to break down the DIBF

By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

particles and then was heated in a conventional oven (at 60°C) for about 10 minutes while the container was sealed. Then the sample was removed from the oven and DIDMA (0.0185 g, $9 \times 10^{-5}\text{M}$) and 8 grams of resin were added separately. After stirring for a few minutes, the sample was returned to the oven and sealed to avoid the loss of any components. After 30 minutes all components were checked for solubility by placing a small amount of the mixture between glass slides and examining for the existence of undissolved particles. The sample between glass slides was observed in the light path of an overhead projector to detect undissolved particles. Samples showing undissolved particles were put back in the oven for another 30 minutes to insure that all components were dissolved completely.

DIBF photoinitiator systems and materials that contain them are relatively stable. They can be stored indefinitely in light opaque containers. Under low levels of light, they are stable and strict darkroom conditions are not necessary for sample preparation. Dim light conditions which still allow for comfortable viewing are safe to maintain the shelf stability of a formulated sample. However, precautions are still best taken when working with such samples.

Samples for photocuring were prepared using glass slides with a 10 mil thick spacer at each end. Anaerobic cured ("closed") samples were made by dropping formulated resin on one glass slide and covering it with another glass slide. Round samples about the size of a penny were thereby formed. Aerobic ("open") samples did not have a glass cover. All of the aerobic and anaerobic samples were cured for 30 seconds at half an inch distance from a 75 W tungsten halogen dental lamp equipped with a fiber optic focus (light intensity: about 1.3 W/cm^2).

In a typical case, the samples were purposely cured for only 30 seconds with a light intensity of 1.3 W/cm^2 . These conditions cure the resins to a relatively low degree of cure (43% to 55%) thus giving a larger margin in which to observe the post cure effect. As a control the same polyester resin containing SGL's initiator system was tested using DSC at both 3 days and 30 days

after being formulated but not cured. No difference in their heats of reaction in DSC testing were observed when 1 wt.% benzoyl peroxide was added. This indicates that no dark reactions occur until after the samples have been cured with light. Also, there are no stability problems in the formulated resins.

DSC Test:

A Perkin-Elmer DSC-4 differential scanning calorimeter was used for DSC studies. Pans were stainless steel large volume capsules (PE numbers 0319-0218). All DSC tests were performed under the same conditions which were as follows: 1) Temperature range: 25-310°C; 2) Heating rate: 20°C/minute; 3) Cooling rate: 320°C/minute; 4) Sample weight: 10-20 mg for cured samples, 3-7 mg for uncured samples. The base line was adjusted before every group of tests.

The heat of reaction of the control resin containing 1% dibenzoyl peroxide was used as the reference (DH_{total}). The percentage of degree of cure of photocured samples was obtained by comparing the heat of reaction on DSC ($DH_{residue}$) with the heat of reaction of the control resin containing 1% peroxide. The calculation is shown by the following equation:

$$a = 1 - DH_{residue}/DH_{total} \quad (9)$$

For all of the samples studied using DSC, only the center parts of the cured polymers were collected. This is the area of the sample which received the most intense light. The weights of the samples were measured to four decimal places. The temperature was raised up to 360°C for some select samples, but no further reactions were observed indicating the polymerization was complete at 310°C.

Results and Discussion

Systematic studies of post cure resulting from an unsaturated polyester resin containing 0.15 wt.% DIBF and coinitiators were performed. A total of 48 samples were tested. Half of them were cured under aerobic and half under anaerobic conditions. Then 12 of each were stored in the dark and 12 of each were stored in room light respectively. We made no change in the conditions under which the samples were cured. Samples cured aerobically were stored in open air whereas samples cured anaerobically were treated accordingly.

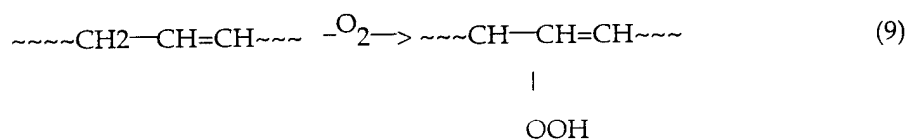
Speed of post cure -- As observed, all of the samples show relatively high rates of post cure within the first few days, after which the process appears to slow down and essentially stop. The likely reasons are that the diffusion of "long lived" radicals formed during the initial cure becomes difficult and there are fewer active sites available as the degree of cure increases. Also, the number of radicals decrease due to scavenging and other "non-productive" steps.

Difference between dark and light stored samples -- In closed samples it is observed that post cure storage under ambient light [shown in Figure 1, (a)] exhibits a higher degree of post cure (82%) than the samples stored in the dark [(63%), shown in Figure 1, (c)] after about 36 days. We believe that unreacted DIBF is excited by ambient radiation and continues to function as an initiator. In addition we postulate that long lived radicals which survive after the initial cure are a second source of radicals for the post cure to occur. Post cure of unsaturated polyesters has been well documented by others (Kerle, Grentzer; Joneja, 1985). Conversely, in the case of the open air samples, those stored in light [shown in Figure 1, (b)] show no obvious differences in the degree of post cure from samples stored in the dark [shown in Figure 1, (d)]. This is probably because of the strong inhibition effect of oxygen which reduces or eliminates the effectiveness of the newly excited radical sources formed from residual initiator and coinitiators. Thus only long lived

radicals and peroxide decomposition (discussed below) are responsible for the observed post cure effect.

The color of the samples stored in room light bleached from a medium yellow color to a pale yellow as time passed. The original medium yellow color of the samples resulted both from unreacted DIBF and from DIBF which formed by reoxidation of the leuco dye formed as a result of the polymerization reactions (Marino, et al., 1994). The samples that were kept in the dark did not exhibit any bleaching thus retaining their original yellow color. The reason the samples stored in ambient light bleached is that available light continued to excite the initiator molecules and they were reduced to the bleached state. This color bleaching phenomenon supports the above hypothesis about the second radical source when the presence of oxygen is eliminated or minimized.

Difference between closed and open samples -- The first initial cure response for the open samples is higher than for closed cure samples (55% vs. 44%, respectively). This is reasonable considering that oxygen plays an important role in the curing or "drying" of alkyd unsaturated polyester resins (O dian, 1991) as outlined below. Except for dissolved oxygen, which could be substantial, closed samples would not participate in this mechanism during initial cure.



The formation of the allylic hydroperoxide is the first step. This is followed by hydroperoxide decomposition leading to various radical formations that promotes crosslinking. Conjugated double bonds undergo cyclic hydroperoxide formation and decomposition leading to

crosslinking. These mechanisms are supported by the fact that unsaturated polyester resins often exhibit relatively tack-free surfaces when cured in open air suggesting that oxygen plays an important role in the cure mechanism, particularly in the initial stage of cure. This is unlike typical free radical acrylate polymerization, such as UV radiation cure, which is inhibited by oxygen especially at the surface open to the air environment resulting in a wet or tacky layer.

Thus there are several competing reactions occurring, summarized later, which effect the post-cure observations.

Limitation on light effect in post-cure -- It is interesting to note (Table 3) that when closed samples were post cured in the dark for 20 days and then exposed for 28 more days to room light, they did not show much improvement in degree of cure over samples that remained in the dark. The polymer thus formed is much softer than the corresponding polymer formed from samples that were continuously kept in room light. The reason for this observation is still under consideration. Possible explanations include chain termination by the amine during storage resulting in fewer available active sites, depletion of the amine necessary for subsequent photocure and an inherent inability of the post cured resin to become "reactivated" due to viscosity, steric effects, etc.

While post cure effects have been observed when unsaturated resins are cured with peroxide, we have also observed such effects when these resins are cured with visible photoinitiator systems such as 5,7-diiodo-3-butoxy-6-fluorone in unsaturated polyester resins with onium salts and DIDMA as coinitiators.

There are various competing and contributing reactions to the post-cure phenomenon. The radicals formed during the initial curing process are stable and can "live" for a substantial period after the initial polymerization. The presence of long lived radicals allows for continued cure with time, irregardless of storage conditions, as the radicals eventually react with the

available sites. The radicals that cause post cure are unidentified but probably similar to those responsible for the post cure in peroxide catalyzed polymerization. Final post-cure observed via this mechanism alone (i.e., without heat, visible initiators, etc.) is expected to reach only a moderate "final" degree of post-cure when starting from a low to medium initial degree of cure. This is primarily due to reduced radical mobility and fewer reactive sites. Another important post-cure scheme is hydrogen peroxide formation followed by its decomposition leading to various radical species that can induce crosslinking. Oxygen thus participates in the curing process, especially in the initial stages of cure, as evidenced in part by tack-free surfaces obtained when samples are cured in open air. This is similar to alkyd resins which are "air-dried". Oxygen is expected, however, to consume radicals formed by other means as is typical of free radical cure mechanisms.

The post-cure effect of unsaturated polyesters cured with typical peroxide initiator systems is a light independent process and can occur whether stored in either the light or the dark. The so-called sunlight post-cure phenomenon has been noted in which the degree of cure increases modestly upon long outdoor exposure. However samples stored in room light with DIBF photoinitiator show an increased rate and extended period of the post cure process if the samples are cured anaerobically. Ambient light excites the initiator forming an additional source of radicals in addition to either long lived radicals or peroxide formed radicals. The observation that these samples reach a higher final degree of post-cure suggests that residual unreacted initiator generates sufficient radicals to promote crosslinking regardless of greater immobility of the network.

Acknowledgment:

The authors wish to express their appreciation to Dr. J. C. Song from the Center for Photochemical Sciences and Dr. Afranio Torres-Filho from Spectra Group Limited for their helpful discussions and assistance. Special thanks are extended to Dustin Martin for his assistance in the data organization and editing of this paper. Dr. James V. Gauchel from Owens-Corning is also acknowledged for his assistance.

Abbreviations:

1. DIBF - 5,7-diiodo-3-butoxy-6-fluorone
2. OPPL - 4-octyloxyphenyl) phenyliodonium hexafluoroantimonate
3. N,N-dimethyl 2,6 di-isopropylaniline (DIDMA)

References:

- Bi, Y.; Marino, T.; Martin, D.; Neckers, D.C. unpublished results; Bi, Y.; Neckers, D.C. *Macromolecules*, 1994, 27, 3683.
- Eaton, D. F. "Dye Sensitized Photopolymerization" *Advances in Photochemistry* Vol. 13, Volman, D. H., Hammond, G. S, and Gollnick, K., Eds. Wiley: NY, 1986.
- Hassoon, S.; Neckers, D. C. *J. Phys. Chem* 1995 99 9416
- Joneja, S.K. Postcuring Changes Polymer Properties, *Research & Development*, March, 1985.
- Kerle, E.J.; Grentzer, T. H. 41st Annual Conference Reinforced Plastics Composite.
- Marino, T.; Martin, D.,; Neckers, D.C. RadTech International Conference, Orlando, Florida, May, 1994.
- Neckers, D.C.; Shi, J. "Fluorone and Pyronin Y Derivatives", U.S. patent pending, Japan pending, EPO pending, designating BE, FR, DE, IT, NL, SW, CH, UK, 07/881,048 5-11-92; Shi, J.; Zhang, X.; Neckers, D. C. *J. Org. Chem.*, 1992., 57, 4418.
- Odian, G.G., *Principals of Polymerization*; Wiley: N.Y., 1991.

Table 1

POST CURE EFFECT (LIGHT STORAGE)

	Time After Cure (Days)									
	0	1	2	6	9	12	15	19	22	36
Closed	44 %	64 %	65 %	68 %		77 %		79 %		82 %
Open	55 %	58 %	64 %		65 %		62 %		67 %	

Comments: (1) 0.15 W% of DIBF; Molar ratio of DIBF : OPPI : DIDMA: 1:2:3

(2) 75W tungsten halogen light source, 30 seconds exposure, 1/2" distance
between lamp and sample.

(2) Polymer feels harder and color becomes bleached with time.

Table 2

POST CURE EFFECT (DARK STORAGE)

	Time After Cure (Days)									
	0	1	2	6	9	12	15	19	22	36
Closed	44 %	57 %	62 %	59 %		57 %		56 %		63 %
Open	55 %	63 %	65 %		66 %		67 %		69 %	

Comments: (1) Sample formulation and cure conditions are the same as those in Table 1.

(2) Polymer becomes somewhat harder with time and the color does not bleach.

Figure 1: Time Effect on Post Cure in Unsaturated Polyester Polymers

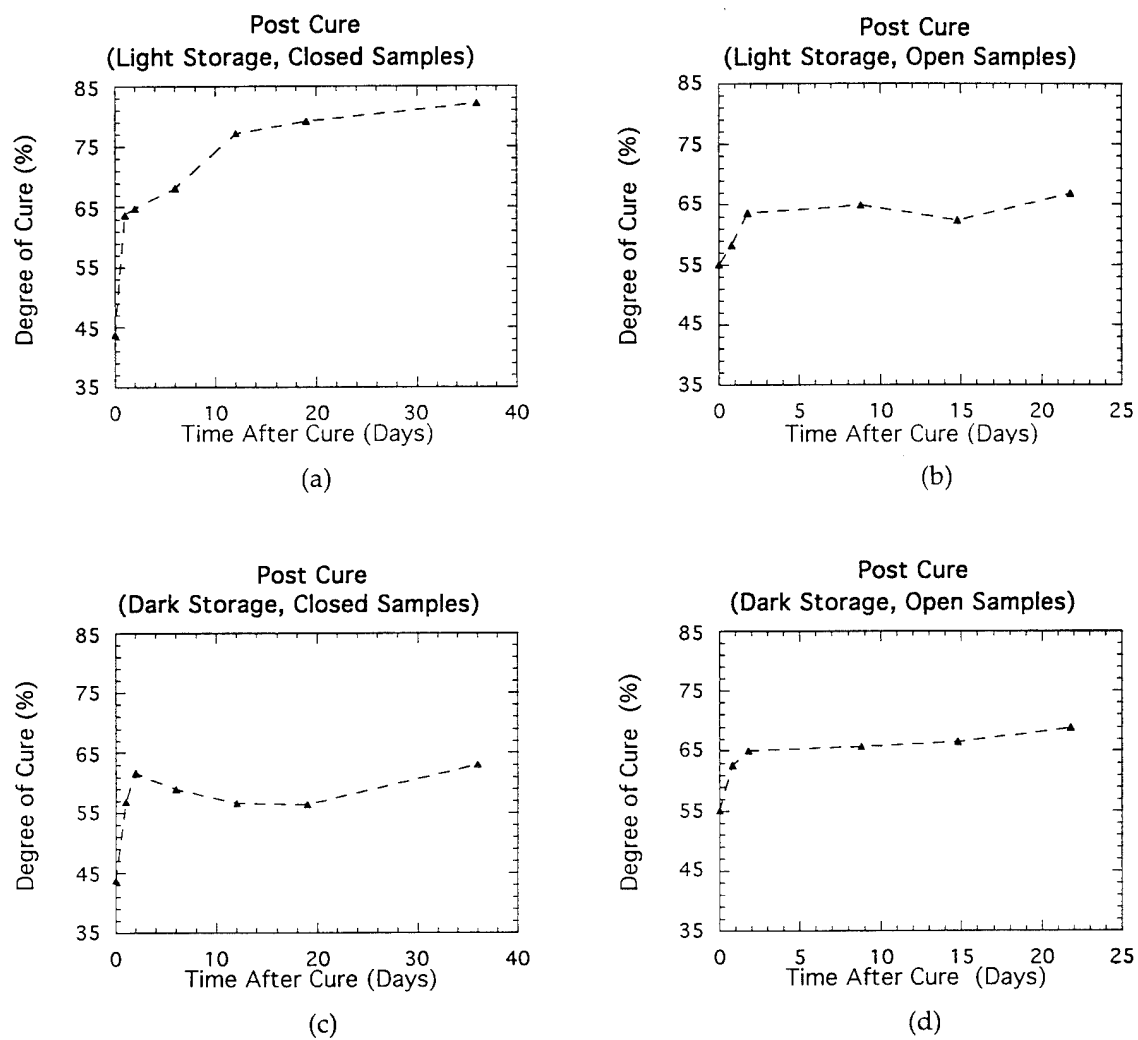


Table 3: Post Cure Effect (Dark Storage Followed by Light)

Degree of Cure					
Immediately After Initial Cure	After 20 Days Dark Storage	Samples were then exposed in Room Light	2 days in Room Light After Dark Storage	6 Days in Room Light After Dark Storage	28 Days in Room Light After Dark Storage
44 %	56 %		58 %	58 %	58 %

Comments: The samples here are exactly the same as in Table 2, entry one. These samples were stored in room light after 20 days dark storage.